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Characterization of Coke from the Catalytic Pyrolysis of Biomass

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Introduction

The conversion of cellulosic biomass to liquid transportation fuels is politically, environmentally and economically advantageous as an alternative to non-renewable petroleum based fuels while retaining investments in existing liquid based fuel infrastructure. In addition to biological techniques, there are two thermochemical methods for producing hydrocarbon rich fuel from biomass. Both pyrolysis and gasification convert carbohydrates to hydrocarbons through a combination of heating and catalytic reactions (Figure 1).

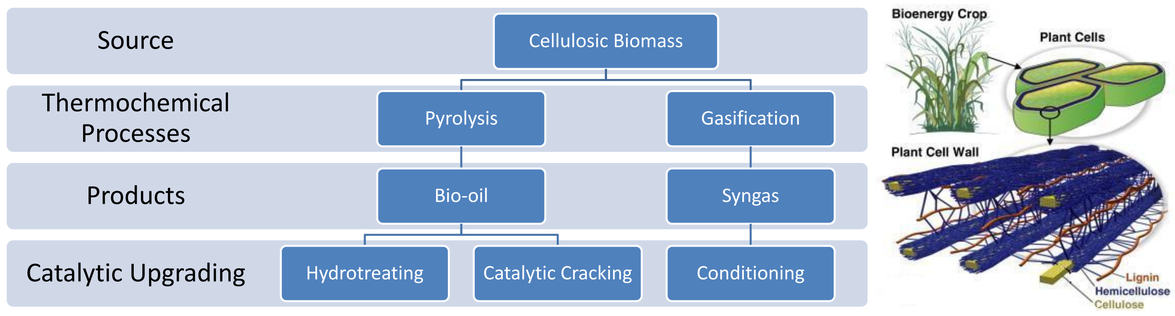

Figure 1. Possible thermochemical pathways of the conversion of cellulosic biomass to refinery ready liquid transportation fuels.

Pyrolysis is the rapid heating of biomass between 400°C and 600°C in the absence of oxygen. The bio-oil produced is chemically unstable and not miscible with conventional fuels due to high oxygen content. In order to produce molecules similar to precursors for hydrocarbon fuels, the use of a catalyst (typically zeolite) is required to reduce the oxygen content. Over the course of catalytic reactions, a problematic carbonaceous deposit called coke forms in the active sites of the zeolite, eventually deactivating the catalyst completely.

This study is modeled after petroleum based zeolite coke characterization research and focuses on understanding the similarities and differences of biomass derived coke. These findings support the purposeful development of strategies to reduce the rate and amount of coke development in thermochemically derived biofuels.

Materials/Methods

Four samples of coke were obtained through the catalytic pyrolysis of pine at 500°C in a fixed-bed micro-reactor with course ground zeolite (ZSM-5) as catalyst. Biomass was continuously fed at approximately .2 g/min. Pyrolysis products were measured by a molecular beam mass spectrometer (MB/MS) in real time. Pyrolysis was stopped at four distinct levels of deactivation described in table 1.

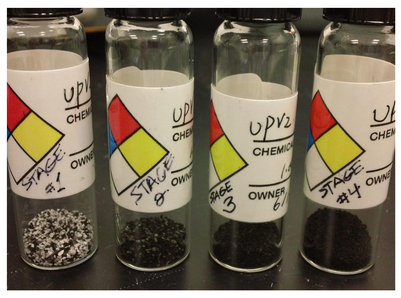

Figure 2. Four samples of zeolite catalyst (white) at varying stages of coke (black) development.

Table 1. Defining features of each stage of coke development, time on stream (TOS) was stopped when key products started or stopped forming, indicating effectiveness of catalyst.

Stage of Deactivation	Products visible on MB/MS when TOS was stopped	Notable compounds (m/z)	TOS (minutes)
1	Upgraded Vapors (UV)	Benzene (78) Toluene (92) p-Xylene (106)	1.5
2	Phenols	Phenol (94) Cresol (108)	3.7
3	Primary Vapors (PV)	Furan (68) 2-methylfuran (82) Furfuryl Alcohol (98) 2-methoxy-phenol (124) 1-hydroxy 2-propanone acetate (132)	7.1
4	No Upgraded Vapors		30.4

Solid samples (Figure 2) were analyzed via:

- Elemental Analysis
- ^{13}C MAS NMR (Nuclear Magnetic Resonance)
- Thermogravimetric Analysis (TGA)

20mL Carbon-tetrachloride (CCl_4)and Methylene-chloride (CH_2Cl_2) soxhlet extractions were done on 50mg of each sample for 4 and 6 hours respectively and 1g samples of stage 2 and 4 for 8 hours. Solutions were analyzed via GC/MS.

Results/Discussion

^{13}C MAS NMR

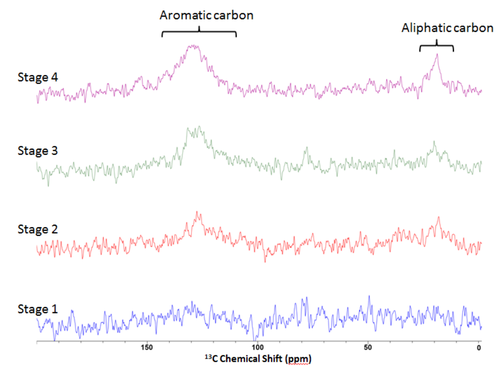

Figure 3. Chemical shift of carbon 13 isotopes in parts per million (ppm) from solid coke samples at four stages of coke development (from Erica Gjersing).

Elemental Analysis

Table 2. Ratios of atoms at four stages of coke development. Percentages are reflective of coke without water and were calculated using both TGA and elemental analysis data.

*Oxygen calculated by difference.

Stage of Deactivation	%C	%O*	%H	%N
1	43	67	-10	.5
2	84	14	1.5	.2
3	89	7	4.3	.1
4	85	11	3.7	.1

Initial solid state NMR confirmed the presence of two types of coke molecules (Figure 3). Based on coke literature, we suspect that larger carbon ring structures (aromatic carbon) form inside catalyst pores while carbon chains (aliphatic carbon) accumulate on the outside of the molecule (Guisnet *et al*, 2009).

Percentage C|H|O|N calculations are representative of coke without water (Table 2). Variable water content was subtracted from coke for each stage via TGA data. Hydrogen to carbon ratios average less than .5 suggesting that coke is very similar to coal. By adding hydrogen donor molecules to the catalytic pyrolysis process, hydrogen atoms could possibly intercept carbon atoms to form more desirable hydrocarbons while simultaneously preventing coke formation.

Thermogravimetric analysis revealed two weight loss events (Figure 4). The first phase occurs under 200°C and represents water loss. The second event consists of two distinct events indicated by the two features in the derivative curve, further confirming two types of coke compounds (Figure 5).

No compounds were found in any stage of the CCl_4 and CH_2Cl_2 extractions on GC/MS before or after condensing solutions. Unlike petroleum based coke formed between 350-450°C, biomass based coke formed between 500-600°C is insoluble in CCl_4 and CH_2Cl_2 (Holmes *et al*, 1996).

Thermogravimetric Analysis

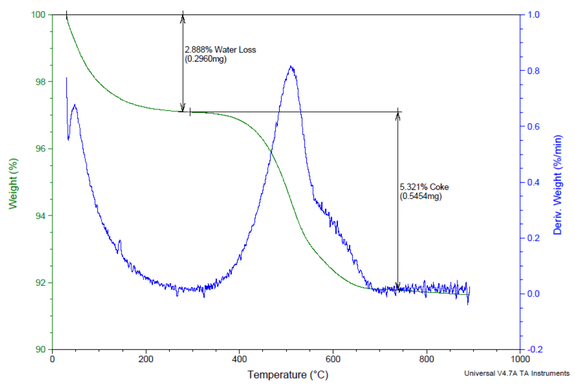

Figure 4. Weight loss (green) and weight loss derivative (blue) of a stage 2 sample. Initial mass loss represents water. Second mass loss represents coke and occurs in two distinct events indicated in the asymmetrical features of derivative curve.

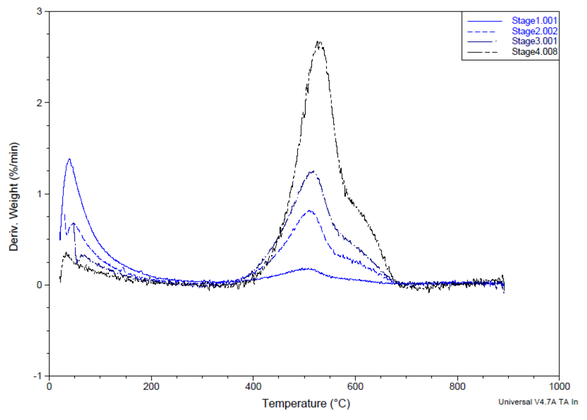

Figure 5. Weight loss derivatives for each stage of deactivation. Asymmetric features indicating two distinct events occur at each stage of coke development.

Future Work

- Use TGA/PTGA in conjunction with a Mass Spectrometer to confirm variable amounts of carbon and hydrogen released at each stage of coking.
- Dissolve zeolite catalyst with hydrofluoric acid in order to analyze remaining insoluble coke in GC/MS.
- Conduct CCl_4 and CH_2Cl_2 extractions on coke samples created at lower pyrolysis temperature (450°C vs. 600°C) and analyze through GC/MS.

Acknowledgements/References

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